

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
25 September 2003 (25.09.2003)

PCT

(10) International Publication Number  
**WO 03/078521 A1**

(51) International Patent Classification<sup>7</sup>: C08K 5/00, 5/10,  
C08L 29/14, B32B 17/10, C08F 8/28, C08J 5/18

(21) International Application Number: PCT/US03/07352

(22) International Filing Date: 11 March 2003 (11.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/363,936 12 March 2002 (12.03.2002) US

(71) Applicant (for all designated States except US): **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WONG, Bert, C.** [US/US]; 212 Hawkes Court, Hockessin, DE 19707 (US). **RYMER, Donald, L.** [US/US]; 4233 School House Road, Little Hocking, OH 45742 (US). **READ, Nolan, K., III** [US/US]; 2 Chadwick Square, Vienna, WV 26105 (US).

(74) Agent: **DOBSON, Kevin, S.**; E.I. DUPONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LOW-COLOR STIFF PVB LAMINATES

(57) Abstract: The present invention describes laminate articles comprising a stiff, low-color PVB sheet having a YID of less than 12 and having a low concentration of plasticizer in the PVB composition, wherein the sheet is prepared from a composition that includes a PVB bleaching compound. A sheet of the present invention is useful for making glass laminates useful for parts in making cars, boats, trains, buildings, display cases, and other articles that utilize transparent glass laminates.

WO 03/078521 A1

**TITLE****LOW-COLOR STIFF PVB LAMINATES**

This application claims the benefit of U.S.

5 Provisional Application No. 60/363,936, filed March 12, 2002.

**BACKGROUND OF THE INVENTION**

Plasticized polyvinyl butyral (PVB) sheet is used in the manufacture of laminate structures such as, for  
10 example: windshields for vehicles including automobiles, motorcycles, boats and airplanes; homes and buildings; shelving in cabinets and display cases; and other articles where structural strength is desirable in a glass sheet. In many applications, it  
15 is desirable that the laminate be transparent and colorless, or at least have very low color. Undesired or unintended color in a glass laminate can be a result of impurities from various sources. In some cases, color can occur in the PVB interlayer. Color in a PVB  
20 sheet can result from several sources in the PVB resin, or from the manufacturing process. For example, color can result from instability of the PVB resin, from impurities, or from other additives present in the PVB composition. Color in a PVB sheet can develop during  
25 storage of the PVB, or be caused by process conditions to which the resin is subjected.

In a conventional PVB sheet manufacturing process, additives can be included to protect PVB from developing color. Examples of such additives are  
30 antioxidants, such as octylphenol, and ultra violet light stabilizers. In some commercial applications, it has been found that combinations of additives can be required for satisfactory results. For example, conventional PVB sheet compositions can include,  
35 Tinuvin® P, Tinuvin® 123 in addition to Tinuvin® 326 to obtain satisfactory light stability in the sheet.

Using combinations of additives can add additional expense and complexity to the manufacturing process, particularly if a change in the additives must be made. For example, in some instances changing the composition  
5 used in a chemical or polymer manufacturing process can have unexpected results. The unexpected results can sometimes be unwanted.

Conventional PVB sheet typically includes a plasticizer in order to increase the flexibility and  
10 processibility of the PVB sheet. Generally, the higher the concentration of plasticizer, the more flexible the sheet. Various plasticizers are conventional in the manufacture of PVB, and include such plasticizers as:  
15 glycol di(2-ethylhexanoate) (3GO) and tetraethylene glycol diheptanoate (4G7), for example. Typically, plasticizer is included in amounts of greater than 30 pph, based on the total dry weight of the resin. Depending upon the application, as well as other  
20 factors, highly plasticized PVB can have as much as 60 pph of plasticizer.

In some special applications, however, it can be desirable to include small amounts of plasticizer so that a stiff PVB sheet can be obtained. One problem  
25 with using low plasticizer concentrations is that the PVB composition may require exposure to higher temperatures in order to extrude the resin and/or to shape the extruded sheet for use in the application for which it was intended. However, when a conventional  
30 PVB resin is exposed to such high temperature, color can develop in the sheet thereby making it unusable in applications where clarity and high laminate transparency are critical.

It can be desirable in the art of manufacturing  
35 PVB laminate articles, to prepare a stiff PVB sheet, wherein the sheet includes a low concentration of

plasticizer, by a process wherein the PVB composition does not develop a high color level upon exposure to high temperatures during extrusion or lamination.

It can also be desirable to obtain PVB sheet by a process wherein the color of the sheet can be improved  
5 by proper selection of additives used in the process.

#### SUMMARY OF THE INVENTION

In one aspect, the present invention is a  
10 plasticized PVB composition consisting essentially of: polyvinylbutyral having a hydroxyl number of from about 15 to about 25; a plasticizer or mixture of plasticizers present in a finite amount of less than about 30 pph based on the dry weight of the resin  
15 composition; a surfactant; and optionally including either (i) a PVB bleaching compound, or (ii) an antioxidant and a UV light stabilizer, or (iii) both (i) and (ii).

In another aspect, the present invention is an  
20 article comprising: a plasticized PVB sheet interlayer wherein the PVB sheet consists essentially of: polyvinylbutyral having a hydroxyl number of from about 15 to about 25; a plasticizer or mixture of plasticizers present in a finite amount of less than  
25 about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB bleaching compound, or (ii) an antioxidant and a UV light stabilizer, or (iii) both (i) and (ii), wherein the interlayer was obtained after  
30 extrusion at a temperature in the range of from about 225°C to about 245°C, and wherein the interlayer has a yellowness index (YID) measurement of less than about 12.

In still another aspect, the present invention is  
35 a laminate article useful as architectural glass and/or as automobile glass, train glass, or boat glass

comprising: a plasticized PVB sheet consisting essentially of less than 30 pph of either 3GO or dibutyl sebacate as plasticizer, wherein the PVB sheet has a glass transition temperature ( $T_g$ ) of from at least about 35°C to 60°C and a YID of less than about 12.

In still another aspect, the present invention is a process for preparing a low color, PVB sheet comprising the steps: (I) admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and a surfactant (II) stabilizing the mixture obtained in step (I) by (a) raising the pH of the mixture to at least pH 10 (b) isolating the resin by draining the liquid, (c) washing the resin with neutral pH water; (III) plasticizing the PVB resin composition with plasticizer in a finite amount of less than about 30 pph based on the dry weight of the PVB resin; (IV) optionally mixing (a) a PVB bleaching compound and/or (b) an antioxidant and a UV light stabilizer with the PVB resin composition; and (V) extruding the PVB sheet at a temperature of from about 225°C to about 245°C to obtain a PVB sheet having a  $T_g$  of from at least about 35°C to 60°C and a YID of less than about 12.

25

#### DETAILED DESCRIPTION

In one embodiment, the present invention is a plasticized PVB sheet composition that includes polyvinylbutyral having a hydroxyl number of from about 15 to about 25, plasticizer in an amount of less than 30 pph based on the dry weight of the PVB resin, and a PVB bleaching compound.

PVB can be manufactured according to known processes. For example, U.S. Patent Number 3,153,009 describes a process for commercial manufacture of PVB. U.S. Patent Number 4,696,971 also describes a process for manufacturing PVB wherein sodium

dioctylsulfosuccinate (DOSS) is used as a surfactant. With some exceptions that will be obvious to one skilled in the art, the teachings of the above-referenced patents are hereby incorporated by  
5 reference.

The PVB composition of the present invention includes the plasticizer in a finite amount, but at a concentration of less than 30 pph, based on the dry weight of the PVB resin. The present invention  
10 preferably includes plasticizer in an amount of from about 5 to about 30 pph, more preferably the plasticizer content is from about 15 to about 30 pph. Even more preferably the plasticizer content is from about 18 to about 28 pph, and most preferably from  
15 about 18 to about 22 pph.

The term flake, as used in the present invention, describes a particular physical form of PVB resin material, that is, granular or particulate versus a film or a sheet. The physical form of the resin does  
20 not necessarily indicate a different PVB composition within the present application, even though sheets and/or films may include additives not found in the resin flake.

Plasticizers of the present invention can be  
25 chosen from any that are known or used conventionally in the manufacture of plasticized PVB sheeting compositions. For example, a plasticizer suitable for use herein can be a plasticizer or a mixture of plasticizers selected from the group consisting of:  
30 diesters obtained from the chemical reaction of aliphatic diols with carboxylic acids, including diesters of polyether diols or polyether polyols; and, esters obtained from polyvalent carboxylic acids and aliphatic alcohols. For convenience, when describing  
35 the sheet compositions of the present invention, a mixture of plasticizers can be referred to herein as

"plasticizer". That is, the singular form of the word "plasticizer" as used herein can represent the use of either one plasticizer or the use of a mixture of two or more plasticizers in a given sheet composition. The  
5 intended use will be apparent to a reader skilled in the art. Preferred plasticizers for use herein are diesters obtained by the reaction of triethylene glycol or tetraethylene glycol with aliphatic carboxylic acids having from 6 to 10 carbon atoms; and diesters obtained  
10 from the reaction of sebacic acid with aliphatic alcohols having from 1 to 18 carbon atoms. More preferably the plasticizer is either 4G7, 3GO or dibutyl sebacate (DBS). Most preferably the plasticizer is 3GO.

15 The composition of the present invention optionally includes at least one PVB bleaching compound. A PVB bleaching compound (bleaching compound) of the present invention is any compound that can reduce or eliminate color from a PVB sheet relative  
20 to the color of an otherwise identical composition, treated using an identical or similar process, with the exception that a bleaching compound is not present. The mode of the bleaching action demonstrated by the bleaching compound is not critical to the present  
25 invention. For example, a bleaching compound useful in the practice of the present invention can be a compound that reacts directly with color-forming compounds (color bodies) present in a PVB sheet composition, or a compound that is capable of yielding a compound that  
30 reacts directly with color-bodies. A bleaching compound can be a compound that can decompose in situ to yield decomposition products capable of reacting with color bodies present in a PVB sheet composition. A bleaching compound in the practice of the present  
35 invention can be a compound that inhibits the formation of color bodies. Bleaching compounds of the present

invention include, for example, inorganic bisulfites such as sodium or potassium bisulfite; organic bisulfites such as tetramethylammonium bisulfite; and compounds similar in structure or function. Bleaching  
5 compounds also include sulfosuccinates such as dialkyl sulfosuccinates. For example, the present invention can include DOSS as a bleaching compound.

A bleaching compound of the present invention can be included in any effective finite amount. An  
10 effective amount for the purposes of the present invention is any amount that reduces the color of a PVB sheet relative to the color of an identical or substantially similar PVB sheet composition without the bleaching compound. Color measurement can be done  
15 according to any conventional standard practice. Alternatively, in the absence of comparative data, an effective amount is any amount that reduces the color of a PVB sheet to a yellowness index (YID) of less than about 12 YID. Preferably the YID is less than about  
20 10, more preferably less than about 8, and most preferably less than about 6.

A bleaching compound can be included in an amount of from about 0.01 to about 0.85 pph, based on the weight of polyvinyl alcohol (PVA) used in the  
25 preparation of PVB. Preferably, the bleaching compound is present in an amount of from about 0.05 to about 0.80 pph, more preferably in an amount of from about 0.10 to about 0.75 pph, and most preferably in an amount of from about 0.15 to about 0.70 pph. While  
30 color reduction in a PVB sheet is an important consideration, the amount of bleaching compound included will also be a function of the cost of production and the other properties that may be affected by including the additive.

35 The present invention includes a surfactant. A surfactant suitable for use herein can be any that is



known to be useful in the art of polyvinylbutyral manufacture. For example, surfactants suitable for use herein include: sodium lauryl sulfate; ammonium lauryl sulfate; sodium dioctyl sulfosuccinate; ammonium  
5 perfluorocarboxylates having from 6 to 12 carbon atoms; sodium aryl sulfonates, adducts of chlorinated cyclopentadiene and maleic anhydride; partially neutralized polymethacrylic acid; alkylaryl sulfonates; sodium N-oleyl-N-methyl taurate; sodium alkylaryl  
10 polyether sulfonates; triethanolamine lauryl sulfate; diethyl dicyclohexyl ammonium lauryl sulfate; sodium secondary-alkyl sulfates; sulfated fatty acid esters; sulfated aryl alcohols; and the like. Preferable surfactants include sodium lauryl sulfate, sodium  
15 dioctyl sulfocuccinate, sodium cocomethyl tauride, and decyl(sulfophenoxy)benzenesulfonic acid disodium salt.

The surfactant can be included in any effective amount for the particular set of process conditions practiced. The surfactant can be included in an amount  
20 of from about 0.01 to about 0.85 pph by weight, based on the weight of PVA used to prepare PVB. Preferably the surfactant is included in an amount of from about 0.10 to about 0.80 pph. More preferably, the surfactant is included in an amount of from about 0.15  
25 to about 0.75 pph. Most preferably, the surfactant is included in an amount of from about 0.15 to about 0.70 pph.

The surfactant and the bleaching compound can be the same compound, or can perform both functions. The  
30 bleaching compound is optional only in the event that the surfactant can also perform the function of a bleaching compound. Otherwise the bleaching compound is considered to be essential in the practice of the present invention. For example, DOSS can be used in  
35 the practice of the present invention as a surfactant. DOSS can also be a bleaching compound in the practice

of the present invention. In one particularly preferred embodiment, DOSS can be included as both a surfactant and as a bleaching compound. In this embodiment, the use of a bleaching compound other than DOSS is optional.

Antioxidants can be optionally included in a PVB composition of the present invention during sheet preparation to inhibit the oxidation of the PVB sheet and/or components. Preferred antioxidants are known conventionally and available commercially. Most preferred are bis-phenolic antioxidants, which are surprisingly more suitable for preparing low color PVB sheeting, particularly when 3GO is used as plasticizer. Bis-phenolic antioxidants are available and can be obtained commercially. Suitable bis-phenolic antioxidants include 2,2'-ethylidenebis(4,6-di-t-butylphenol); 4,4'-butylidenebis(2-t-butyl-5-methylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol); and 2,2'-methylenebis(6-t-butyl-4-methylphenol), for example. Bis-phenolic antioxidants are commercially available under the tradename of ANOX™ 29, LOWINOX® 22M46, LOWINOX® 44B25, and LOWINOX® 22IB46, for example.

An antioxidant can be included in any effective finite amount. Preferably, the antioxidant is included in an amount of from about 0.01 to about 0.6%, based on the total weight of the sheet. More preferably, the antioxidant is present in amount of from about 0.03 to about 0.3%, most preferably in an amount of from about 0.05 to about 0.25%.

Other additives are known conventionally to be useful, and can be included in a sheet composition of the present invention. Such additives include: light stabilizers, particularly UV light stabilizers, such as Tinuvin® P; Tinuvin® 326, and Tinuvin® 123. UV light stabilizers can stabilize the PVB composition by

absorbing ultraviolet light and preventing unwanted effects by the UV light on the PVB. Adhesion control agents such as alkali and alkaline earth metal salts of carboxylic acids, alkaline earth metal salts of inorganic acids, or a combination of such salts can be added. Surface tension controlling agents such as Trans® 290 or Trans® 296 available from Trans-Chemco; or Q2-3183A® available from Dow Chemical can be used in the practice of the present invention. The use of Trans® 290 or Trans® 296 is preferred.

A PVB resin of the present invention can be obtained by processes known in the art of PVB manufacture. PVB resins used in the practice of the present invention can be prepared by mixing PVA with butyraldehyde in an aqueous medium in the presence of an acid or mixture of acids, at a temperature of from 5°C to 100°C.

Typically, the ratio of PVA to butyraldehyde can be chosen such that the PVB has residual hydroxyl functionality, conventionally reported as OH number. Residual hydroxyl functionality can vary according to what properties are desirable in the PVB. The relative amounts of butyraldehyde and PVA required to obtain the desired OH number in the PVB resin will be readily apparent to those skilled in the art of PVB manufacture. In the practice of the present invention residual hydroxyl can be in the range of from about 14 to about 30. Preferably, the OH number is from about 15 to about 25. More preferably, the OH number is from about 15 to about 20, and most preferred in the practice of the present invention is PVB resin having an OH number in the range of from about 17 to about 19. The OH number can be determined according to standard methods such as ASTM D1396-92.

In a preferred embodiment, a low color PVB sheet of the present invention can be obtained by a process

comprising the steps: (I) admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and a surfactant (II) stabilizing the mixture obtained in step (I) by (a) raising the pH of the mixture to at least pH 10 (b) isolating the resin by draining the liquid, (c) washing the resin with neutral pH water; (III) plasticizing the PVB resin composition with from about 10 to about 30 pph of plasticizer based on the dry weight of the PVB resin; (IV) optionally mixing (a) a PVB bleaching compound and/or (b) an antioxidant and a UV light stabilizer with the PVB resin composition; and (V) extruding the PVB sheet composition at a temperature of from about 225°C to about 245°C to obtain a PVB sheet having a  $T_g$  in the range of from about 35°C to about 60°C, and a YID of less than about 12.

The steps of the process described herein can be carried out in varied order. For example, while it can be necessary to carry out step (I) before step (II) it is not essential, for the purpose of obtaining a low color sheet of the present invention, that steps (III) or (IV) be carried out in any particular order. Although it may be preferable to implement these steps just prior to, or simultaneous with, step (V). Also, the order of addition of components is not critical in the practice of the present invention, although a skilled artisan will recognize that there may be other benefits of carrying out the process in a consistent and ordered manner. For example, plasticizer can be mixed with the PVB either before or during the extrusion of the PVB composition, as described in U.S. Pat. No. 5,886,075.

Plasticizer can be added in any amount desirable to obtain a plasticized PVB composition. To obtain a stiff PVB sheet in one embodiment of the present invention, plasticizer is added in an amount of less

than about 30 pph, based upon the total dry weight of the resin. The "dry weight" as used herein refers to the weight of the resin after water has been removed from the resin.

5       The glass transition temperature ( $T_g$ ) of a PVB sheet is dependent in part upon the concentration of plasticizer included in the composition. A PVB sheet useful in the practice of the present invention has a  $T_g$  of from about 35°C to about 60°C, as measured by  
10   Dynamic Mechanical Analysis ASTM D4065 (DMA), using the tangent delta (phase shift at 1 Hz) data as indicator. Preferably, the  $T_g$  is from about 40°C to about 57°C, more preferably from about 45°C to about 57°C, most preferably from about 50°C to about 55°C.

15       In one of the preferred embodiments of the present invention, a stiff PVB sheet can be obtained having low color and low concentration of plasticizer. For sheet having low concentration of plasticizer, it can be necessary to extrude the sheet at a higher temperature  
20   than when using higher amounts of plasticizer. For example, PVB resin plasticized with from about 5 to about 30 pph plasticizer can be extruded at a temperature of from about 225°C to about 245°C. Preferably the resin can be extruded at a temperature  
25   of from about 227°C to about 245°C. More preferably, the resin can be extruded at a temperature of from about 228 °C to about 242°C, and most preferably from about 230°C to about 240°C.

30       A low color PVB sheet suitable for the purposes herein can be obtained by a process that comprises the steps of: (1) isolating PVB flake from a PVA/butyraldehyde reaction mixture previously described herein; (2) optionally admixing an antioxidant and a UV light stabilizer with the plasticizer to obtain a  
35   plasticizer/additive mixture (plasticizer mixture); and (3) co-extruding the flake, plasticizer, antioxidant,

and UV light stabilizer, or alternatively co-extruding the flake and the plasticizer mixture at a feed ratio of plasticizer mixture to dry of flake from about 5:100 (wt:wt) to about 30:100 (wt:wt) at a temperature of  
5 from about 225°C to about 245°C to obtain a low-color PVB sheet having a YID of less than about 12. It is preferable to admix the antioxidant/UV light stabilizer with the plasticizer prior to extrusion of the sheet.

In still another embodiment, a laminate article  
10 can be obtained from a PVB sheet of the present invention. Procedures for preparing glass/PVB laminates are well known in the art, and a skilled artisan would be able to construct a laminate from the presently claimed PVB sheet. A glass/PVB laminate  
15 article as claimed in the present invention can be obtained, for example, by bringing the surfaces of the PVB and glass into contact, pressing the surfaces together at ambient temperature, and then removing air from the laminate structure in an autoclave. The  
20 surface of the PVB can be roughened to facilitate removal of air from the laminate. Other procedures are known and used conventionally. While PVB/glass laminates are described herein, PVB can be used as interlayer material for laminating to other plastic  
25 materials such as polyesters or ionomeric sheeting, for example.

Laminates of the present invention can be useful in various applications for protection from the environment in architectural applications, and/or in  
30 vehicles such as automobiles, boats and trains. Architectural uses for stiff PVB laminates of the present invention include, but are not limited to: external uses such as external windows on buildings, external doors, partitions; internal uses such as  
35 office windows, office doors, glass partitions, table tops, shelves, cabinet doors, protective covers for

tables, room dividers, picture frame glass, display cabinets, display cases, and the like. In vehicles, uses for laminates of the present invention include, but are not limited to: windshields; light covers; 5 body glass, such as sun roof, moon roof, and/or side windows; internal doors; partitions; cabinet doors, and the like. Transparency and clarity are important considerations in applications such as these. Just as important is the protection afforded by the interlayer 10 against splintering and expulsion of glass particles in the event of accidental or intentional impact against the glass laminate.

Laminates of the present invention can include an additive to block the transmission of UV light through 15 the laminate. The additive is preferably the same additive as the UV light stabilizer. UV light is preferably absorbed by the laminate so that less than 10% of UV light is transmitted through the laminate. Preferably less than 8% of the UV light is transmitted 20 through the laminate, more preferably less than 6% UV light is transmitted, and most preferably less than 3%.

PVB interlayers of the present invention have a thickness of greater than 0.254 mm. Preferably, PVB interlayers of the present invention have a thickness 25 in the range of from about 0.254 mm to about 1.6 mm. Multiple layers of PVB can be laminated together or in alternate layers of a laminate. Such multilayer laminates can have PVB interlayers that have a total thickness of greater than 1 mm. Where it is desirable 30 to obtain a laminate wherein the total interlayer thickness is at least 1 mm thick, the YID of the interlayer should not be greater than 12, because the transparency of the laminate can be substantially reduced.

35 In the present application, the term flake can be used to describe a particular physical form of PVB

resin material, that is, granular or particulate versus a film or a sheet. The physical form of the resin does not necessarily indicate a different PVB composition within the present application, even though  
5 sheets and/or films may include additives not found in the resin flake.

### EXAMPLES

The following Examples and comparative examples  
10 are presented to further illustrate the present invention. The Examples are not intended to limit the scope of the invention in any manner, nor should they be used to define the claims or specification in any manner that is inconsistent with the invention as  
15 claimed and/or as described herein.

Analytical tests for Hydroxyl number and YID were performed for each of the examples and comparative examples according to the methods below.

20

Hydroxyl number: ASTM D 1396-92.

Sheet yellowness index (YID)

A PVB chip is made with 21.0 grams of sheet, and heat  
25 pressed into a 10.0 mm thick disk of 50.8 mm diameter. Chip preparation involves preheating a stack of 50.8 mm disks cut from the sheet in a mold for one minute at 2200 N force and 185°C, then increasing the pressing force to 32,000 N at 185°C for two minutes, and cooling  
30 under the same force for 7.5 minutes. No residual surface pattern that was on the extruded sheet is visible in the chip. Yellowness index was determined per ASTM D1925-70 on the 10.0 mm thick chip.

35 Glass Transition Temperature -  $T_g$  is determined by DMA using the procedure of ASTM D4065, using the tangent delta at 1Hz.

#### Example 1

40 Poly(vinyl butyral) sheet was prepared as follows:  
at 90°C, a mixture comprising 32 parts by weight of



poly(vinyl alcohol) of average degree of polymerization 618 and 99.5% hydrolyzed and 68 parts by weight of PVA of average degree of polymerization 1005 and 99.5% hydrolyzed was dissolved in 615 parts by weight of demineralized water. To this solution was added 1 part by weight of 88% para-toluene sulfonic acid and enough sulfuric acid to bring the dissolved PVA solution to a pH of 2. Using the procedure described in US Patent 3,153,009, 62 parts by weight of n-butyraldehyde and 0.47 parts by weight of 70% DOSS and the PVA solution were charged into a vessel maintained at 90°C. After a one hour hold time, a slurry was obtained and the slurry was stabilized with a sodium hydroxide solution to raise the pH to 11. Concurrent with the stabilization, 0.07 parts by weight Trans<sup>®</sup> 290 surface tension stabilizing agent was added. The slurry was then washed and cooled with demineralized water. A granular, white PVB resin with residual hydroxyl number of 18.6 was obtained. The flake was mixed with 3GO plasticizer containing 4 grams per liter of Tinuvin<sup>®</sup> P and 8 grams per liter of Lowinox<sup>®</sup> 44B25 antioxidant and was extruded so that the residence time in the extrusion system was about 15 to 25 minutes. The feed rate ratio of plasticizer to dry flake was 35:100 (wt:wt). Potassium formate solution was injected so as to deliver a potassium concentration of 10 parts per million (ppm) in the sheet. Melt temperature measured at the slot die was between 210 and 215°C. Sheet YID was 5.85.

Example 2

PVB sheet was made in the manner as in Example 1, except that the feed ratio of the plasticizer to dry PVB flake was 20:100, and the melt residence time was 5 25 to 40 minutes. Melt temperature at the die was 233°C. Sheet yellowness index was 5.05.

Comparative Example C1

PVB flake was prepared as in Example 1 except that 10 0.4 parts by weight of sodium lauryl sulfate was used in the place of DOSS as the surfactant, and no other surface tension modifiers were added. A granular, white PVB resin with residual hydroxyl number of 18.6 was obtained. Using the flake made with sodium lauryl 15 sulfate as described here, sheet was prepared as in Example 1. Melt temperature measured at the slot die was between 210 and 213°C. Sheet yellowness was 25.05.

Comparative Example C2

20 The flake described in Example C1 was used to prepare sheet as in Example 1, except that the feed rate ratio of 3GO plasticizer to dry resin of 24:100, and the potassium level in the sheet was 50 ppm, and the melt residence time in the system was 25-40 25 minutes. Melt temperature at the die was between 228 and 233°C. Sheet yellowness was 53.82.

**WHAT IS CLAIMED IS:**

1. A plasticized PVB composition consisting essentially of: polyvinylbutyral (PVB) having a hydroxyl number of from about 15 to about 25; a plasticizer or mixture of plasticizers present in a finite amount of less than about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB bleaching compound, or (ii) an antioxidant and a UV light stabilizer, or (iii) both (i) and (ii).
2. The composition of Claim 1 wherein the plasticizer is 3GO.
3. The composition of Claim 2 wherein the plasticizer is dibutyl sebacate.
4. The composition of Claim 3 wherein the composition includes a bleaching compound, an antioxidant, and a UV light stabilizer.
5. The composition of Claim 4 wherein the bleaching compound and the surfactant are the same compound.
6. The composition of Claim 5 wherein the surfactant is DOSS.
7. The composition of Claim 6 wherein the antioxidant is 2,2'-methylenebis(6-t-butyl-4-methylphenol).
8. The composition of Claim 7 wherein the plasticizer is present in an amount of from about 5 to about 30 pph.

9. The composition of Claim 8 wherein the plasticizer is present in an amount of from about 15 to about 30 pph.

5 10. The composition of Claim 9 wherein the plasticizer is present in an amount of from about 18 to about 28 pph.

10 11. The composition of Claim 10 wherein the plasticizer is present in an amount of from about 18 to about 22 pph.

12. An article comprising at least one layer of the PVB composition of any of Claims 1-11.

15 13. The article of Claim 12 wherein the interlayer has a yellowness index (YID) of less than about 12 and wherein the interlayer was obtained by a process comprising the step: extrusion of PVB sheet at  
20 a temperature in the range of from about 225°C to about 245°C.

14. The article of Claim 13 wherein the article is a laminate comprising at least one layer of PVB and  
25 at least one layer of glass wherein the PVB layer has a thickness in the range of from about 0.254 mm to about 1.6 mm.

15. The article of Claim 14 wherein the laminate  
30 comprises more than one PVB interlayer, and wherein the combined thickness of the PVB interlayers is in the range of from about 0.75 to about 1.6 mm.

16. The article of Claim 14 wherein the laminate  
35 is useful as: architectural glass; automobile glass; train glass; or boat glass.

17. The article of Claim 16 wherein the laminate is useful in an automobile, train, or boat as a: windshield; light cover; body glass, such as sun roof, moon roof, or back and/or side window; internal door; cabinet; cabinet door; partition, and the like.

18. The article of Claim 17 wherein the article is an automobile windshield, light cover, moon roof, sun roof, or back and/or side window.

19. The article of Claim 18 wherein the laminate is useful for: external windows on buildings; external doors; partitions; office windows; office doors; glass partitions; table tops; shelves; cabinet doors; protective covers for tables; room dividers; picture frame glass; display cabinets; display cases, and the like.

20. The article of Claim 12 wherein the laminate is obtained by a process comprising the steps: (i) bringing a PVB polymer interlayer and a glass plate into contact; (ii) removing air from between the glass and the interlayer; and (iii) applying heat and external pressure to adhesively bond the glass plate to the interlayer.

21. A process for preparing a low color PVB sheet comprising the steps: (I) admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and a surfactant (II) stabilizing the mixture obtained in step (I) by (a) raising the pH of the mixture to at least pH 10 (b) isolating the resin by draining the liquid, (c) washing the resin with neutral pH water; (III) plasticizing the PVB resin composition with from about 30 to about 50 pph of plasticizer based on the

dry weight of the PVB resin; (IV) optionally mixing (a)  
a PVB bleaching compound and/or (b) an antioxidant and  
a UV light stabilizer with the PVB resin composition;  
and (V) extruding the PVB composition at a temperature  
5 of from about 225°C to about 245°C to obtain a PVB  
sheet having a  $T_g$  in the range of from about 35°C to  
about 60°C, and a YID of less than about 12.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/07352

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C08K5/00 C08K5/10 C08L29/14 B32B17/10 C08F8/28 C08J5/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 B32B C08L C08F C08K C08J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 036 775 A (SEKISUI CHEMICAL CO LTD) 20 September 2000 (2000-09-20) claims 1,2,5 ---	1,2,12
X	US 5 187 217 A (DEGEILH ROBERT ET AL) 16 February 1993 (1993-02-16) claims 1-3,7 ---	1
A	US 5 886 075 A (FOSS RAY V ET AL) 23 March 1999 (1999-03-23) cited in the application example 1 ---	1-21
A	US 4 696 971 A (DEGEILH ROBERT) 29 September 1987 (1987-09-29) cited in the application claims 1,4,8,14 --- -/--	1-21
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search  9 July 2003		Date of mailing of the international search report  17/07/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Rose, E

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/07352

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 61243 A (FUGIEL RICHARD ANTHONY WALTER ;DU PONT (US); WONG BERT C (US); TUR) 2 December 1999 (1999-12-02) claims 1,7,8 -----	1-21
A	US 5 322 875 A (DAGES DANIEL) 21 June 1994 (1994-06-21) examples -----	1-21



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/07352

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1036775	A	20-09-2000	AU 744658 B2	28-02-2002
			AU 5999999 A	17-04-2000
			BR 9907136 A	03-10-2000
			CA 2312914 A1	06-04-2000
			DE 69906926 D1	22-05-2003
			EP 1036775 A1	20-09-2000
			US 6383647 B1	07-05-2002
			EP 1291333 A1	12-03-2003
			WO 0018698 A1	06-04-2000
			TW 469263 B	21-12-2001
			US 2002136906 A1	26-09-2002
			ZA 200002424 A	14-11-2000
US 5187217	A	16-02-1993	FR 2613370 A1	07-10-1988
			DE 3850803 D1	01-09-1994
			DE 3850803 T2	16-02-1995
			EP 0287416 A1	19-10-1988
			JP 1993187 C	22-11-1995
			JP 7025812 B	22-03-1995
			JP 64000104 A	05-01-1989
US 5886075	A	23-03-1999	WO 9628504 A1	19-09-1996
			AT 194638 T	15-07-2000
			DE 69518015 D1	17-08-2000
			DE 69518015 T2	22-03-2001
			DK 815166 T3	23-10-2000
			EP 0815166 A1	07-01-1998
US 4696971	A	29-09-1987	FR 2547589 A1	21-12-1984
			AT 31193 T	15-12-1987
			BR 8402821 A	21-05-1985
			CA 1245397 A1	22-11-1988
			DE 3467896 D1	14-01-1988
			EP 0130872 A1	09-01-1985
			ES 8503692 A1	16-06-1985
			JP 1786435 C	10-09-1993
			JP 4073445 B	20-11-1992
			JP 60042402 A	06-03-1985
WO 9961243	A	02-12-1999	WO 9961243 A1	02-12-1999
			AU 7594298 A	13-12-1999
			CA 2330071 A1	02-12-1999
			DE 69809801 D1	09-01-2003
			EP 1094939 A1	02-05-2001
			JP 2002516201 T	04-06-2002
US 5322875	A	21-06-1994	FR 2632315 A1	08-12-1989
			DE 68919381 D1	22-12-1994
			DE 68919381 T2	11-05-1995
			EP 0346199 A1	13-12-1989
			ES 2064467 T3	01-02-1995
			FI 892771 A	08-12-1989
			JP 2032149 A	01-02-1990
			JP 2788483 B2	20-08-1998
			KR 157972 B1	15-01-1999

**THIS PAGE BLANK (USPTO)**